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ABSTRACTS

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On the Optical Properties of the Fermentation Lactic Acids.

Part III.—The action of the inactive lactic acid-producing organisms upon the optically active lactic acids added to the fermentation liquids. (pp. 281~283): By Hideo KATAGIRI and Kakuo KITAHARA. (Agr. Chemical Laboratory, Kyoto Imp. University.)

In the present paper, experiments were further carried out with *dl*-lactic acid formers, in order to ascertain the velocity of the racemisation of optically active lactic acids previously added to the fermentation liquids.

With *Lactobacillus plantarum* sp., the velocity of racemisation was observed to be different according to the forms of lactic acid: the *dl*-former was found to reveal as *d*-former against to *l*-lactic acid, while the racemisation of *d*-lactic acid was taken place more rapidly than the organism would reveal as *l*-former.

The direct racemisation of *d*-lactic acid was therefore suggested to be taken place, and the racemisation of *l*-lactic acid was concluded to be positive or indirect with the *dl*-former.

It is interesting to be found that the action of *Lactobacillus pentoaceticus* (*dl*-former) was different from *Lactobacillus plantarum* sp. against to optically active lactic acids; it revealed direct racemisation of *l*-lactic acid, while indirect racemisation of *d*-lactic acid was taken place with the *dl*-former.

Untersuchungen von Essigbakterien aus Formosa. (VIII). (S.

285~307): Von Shosuke TANAKA. (Department of Industry, Government Research Institute, Taiwan, Japan.)

Über ein neues Kristallinisches Diterpen "Sciadopiten" aus dem Blatt- und Zweigöl von *Sciadopitys Verticillata* S. et Z. (II. Mittel.)—Über die Derivate des Sciadopiten und die Reduktion der zwei Isomeren. (S. 308~312): Von Kitsuzi NISHIDA und Hidetaka UOTA. (Holz-chemisches Institut, Kyushu Kaiserliche Universität, Fukuoka, Japan).

In der vorigen Abhandlung wurde gezeigt, dass ein neues kristallinisches Diterpen aus dem Blatt- und Zweigöl von *Sciadopitys* S. et Z. isoliert wurde, das wir Sciadopiten benannten; es geht beim Kochen mit verdünnter Schwefelsäure oder dessen Hydrochlorid durch HCl-Abspaltung zu einem Isomer über; wir geben ihm den Namen Isosciadopiten. Es stellt aus heissem Alkohol lange durchsichtige Prismen dar und schmilzt bei $108\sim 109^{\circ}$. $[\alpha]_D^{20} = +22,13^{\circ}$ (in Chloroform). In Alkohol, Methanol und Eisessig löst es sich in der Kälte schwer, aber ist in verschiedenen organischen Solvenzien leicht löslich.

Dessen Nitroschlorid und Nitrosat bleiben gegenüber denen des Sciadopitens nur in grüner Lösung flüssig und beide kann man nicht kristallisieren lassen.

Das unter starker Abkühlung mit getrocknetem Chlorwasserstoff dargestellte Hydrochlorid scheidet sich aus Methanol und Aether in schönen, farblosen, glänzenden Schuppen ab. Es fängt bei ca. 100° an zu sintern und schmilzt bei $106\sim 108^{\circ}$ unter Schäumen. $[\alpha]_D^{20} = +3,96^{\circ}$ (in Benzol). In der Analyse stimmt es mit Monohydrochlorid überein. Bei der Mischprobe mit Sciadopitenmonohydrochlorid ändert sich sein Verhalten des Schmelzens nicht. Beim Kochen mit alkoholischem Kaliumacetat spaltet es wieder Salzsäure ab, wobei Isosciadopiten regeneriert wird.

Während die verschiedenen Anlagerungsprodukte und die Jodzahl des Sciadopitens und auch das HCl-Anlagerungsprodukt des Isosciadopitens, wie schon erwähnt, einer Doppelbindung entsprechen, versuchten wir noch verschiedene Reduktionen, um festzustellen, wieviel Doppelbindungen die beiden Isomeren wesentlich enthalten und in welcher Beziehung diese eventuell zueinander stehen.

Zunächst reduzierten wir jedes mit Natrium und Alkohol, aber sie regenerierten nur unverändert. Aus diesen Tatsachen geht hervor, dass weder Sciadopiten noch Isosciadopiten eine konjugierte Doppelbindung enthält.

Um die Dihydroverbindung dann aus Monohydrochlorid durch Umsetzen des Chloratoms gegen das Wasserstoffatom herzustellen, wurde Hydrochlorid mit Natrium und absolutem Alkohol reduziert; dabei erhielten wir wider Erwarten nur Isosciadopiten und konnten unser Ziel nicht erreichen.

Bei der katalytischen Hydrierung in Aceton-Lösung unter Verwendung von Platinschwarz absorbierten sowohl Sciadopiten als auch Isosciadopiten die Wasserstoff-Äquivalenz für eine Doppelbindung unter Bildung eines und

desselben Dihydroderivates. Nach Umkristallisieren aus heissen Alkohol lieferte Dihydrosciadopiten farblose lange Tafeln von Smp. $71\sim 72^\circ$. $[\alpha]_D^{20} = +22,87^\circ$ (in Chloroform).

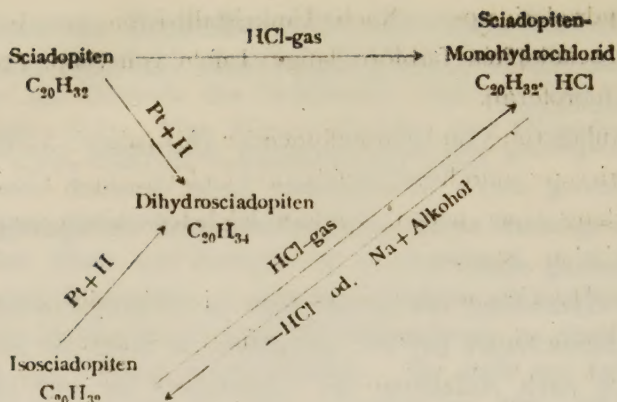
Bei der Anlagerung und darauffolgenden Abspaltung von Salzsäure oder bei der Isomerierung durch Schwefelsäure findet demnach keine Ringsprengung und Bildung einer neuen, sondern höchstens Verlagerung der vorhandenen Doppelbindung statt.

Wurde die Hydrierung des Sciadopitens in Eisessig-Lösung unter Verwendung von Platinschwarz bei 70° ausgeführt, so hörte die Absorption von Wasserstoff auch nach Aufnahme des Äquivalents für eine Doppelbindung auf, und es entstand eine gleiche Dihydroverbindung. Beim weiteren Schütteln dieser Dihydroverbindung in Eisessig-Lösung mit hochaktivem Platinschwarz wurde kein Wasserstoff mehr absorbiert. Dihydrid zeigt in Chloroform-Lösung mit Tetranitromethan keine Färbung.

Aus diesen Ergebnissen geht hervor, dass sowohl Sciadopiten als auch Isosciadopiten nur eine Doppelbindung enthalten, die nicht wie z.B. an einem kondensierenden Teil des Rings, sondern an einer reaktionsfähigen Stelle haftet; also müssen sie tetracyclisches Diterpen und in Beziehung des geometrischen Isomer zueinander stehen.

Folgende Tabellen zeigen die Schmelzpunkte und die spezifischen Drehungsvermögen der Derivate der beiden Isomeren und die oben erwähnten Reaktionen.

	Sciadopiten	Isosciadopiten
Smp.	$95\sim 96^\circ$	$108\sim 109^\circ$
$[\alpha]_D^{20}$	$+11,06^\circ$ (in Chlorof.)	$+22,13$ (")
Monohydrochloride		
Smp.	106°	$106\sim 108^\circ$
$[\alpha]_D^{20}$	$+7,77$ (in Benzol)	$+3,96$ ("),
HI-Abspaltungsprodukt		
Smp.	$108\sim 109^\circ$	$108\sim 109^\circ$
$[\alpha]_D^{20}$	$+22,13^\circ$ (in Chlorof.)	"
Nitrosochlorid		
Zersp.	136°	Flüssigkeit
Nitrosat		
Zersp.	$126\sim 127^\circ$	Flüssigkeit
Dihydrid		
Smp.	$71\sim 72^\circ$	$71\sim 72^\circ$
$[\alpha]_D^{20}$	$+22,87^\circ$ (in Chlorof.)	"



Sulphates and Chlorides as Fertilizers. (VII).—Influence of both salts on the physical constitution of paddy soil annually fertilized with the same manures for five successive years. (pp. 313 ~ 319): By Isenosuke ONODERA and Hiroshi HASEGAWA. (Morioka Agricultural College.)

1. The paddy soils (alluvial loam) of cylinder experiment, which were manured with different combination of sulphates (ammonium sulphate, potassium sulphate), chlorides (ammonium chloride, potassium chloride), sodium phosphate, calcium superphosphate, farmyard manure etc., were found to contain much more of fine and coarse sands and less of clay as compared to that of unmanured soils. But no such definite relation was found to exist in the case of silt.

2. Clay found in soils of chloride plots was in larger proportion than that of sulphate, but silt and fine sand were just the opposite. The amount of fine sand showed no clear relations between both salts.

3. Farmyard manure seems to compensate the minute soil particles, which will dissolve away by the use of chloride fertilizer.

Studies on the Amylase of Yeast. VII.—On the Enzym-chemical Properties. (4). Effects of Hydrogen-ion Concentration on the Durability and Stability of Yeast-amylase during its Storage. (pp. 320 ~ 327): By Kazuki OHNO. (Biochemical Laboratory of Taihoku Imperial University, Japan.)

On the Inorganic Constituents of Green-Manure Crops.
(I). (pp. 328~342): By Kametaro KONISHI and Toshihisa TSUGE. (Agr. and Forest Chemical Laboratory, Kyoto Imperial University).

On the Regeneration of Fibroin (II).—Dispersion of Fibroin. (pp. 343~347: By Takayoshi TANIZAKI. (Agr. Chemical Laboratory, Imperial University, of Tokyo Japan.)

Studies on the Constituents of the Mulberry Leaves, especially on the Protein. Part XI.—A Comparative study on the Distribution of Amino-acids of Mulberry Leaf Proteins. (pp. 348~362): By Yuki-taro KISHII. (At the Katakura Research Institute of Mulberry Culture, near Hachioji City, Tokyo Prefecture, Japan).

Résumé

(1) I have made a comparative study of the distribution of amino-acid by Van Slyke method, tryptophane and cystine of the various proteins contained in the mulberry seeds and leaves. I have studied the differences of the distribution of amino-acids of the protein, soluble in 60% boiling alcohol containing 0.3% of sodium hydroxide, which is the main constituent of the mulberry leaf proteins, from globulin, glutelin and albumin of the mulberry trees; and the changes in the distribution of amino-acids of the total proteins in accordance with the growth of the leaves have also studied.

(2) In the distribution of amino-acids, the protein soluble in the alkaline alcohol of the mulberry leaves distinctly differs from the globulin, glutelin and albumin of the mulberry seeds and leaves; it is a different kind of protein. The alkaline-alcohol-soluble protein has less of amide N, and of total N of diamino-acids, more of total N of monoamino-acid and, it appears, of humin N than the globulin, glutelin and albumin of the mulberry seeds and leaves. Of the total N of diamino-acids fraction, it has far less of arginine N and cystine N and has nearly the same rate of histidine N and lysine N. It has more of monoamino N and, it seems to me, of non-amino N, of the total N of the monoamino-acids fraction.

(3) The alkaline-alcohol-soluble protein has less of tryptophane and cystine than the globulin, glutelin and albumin.

(4) As the proteins of the mulberry leaves are mainly constituted with the alkaline-alcohol-soluble protein, the distribution of the amino-acids of the total protein of the leaves is near to that of the alkaline-alcohol-soluble pro-

tein. The changes in the distribution of the amino-acids of the total proteins in accordance with the growth of the mulberry leaves, show the changes in their qualities. That is to say, the total proteins of the young mulberry leaves, have more of the total N of diamino-acids, and of amide N, and less of the total N of monoamino-acids, of humin N, and of N insoluble in hydrochloric acids than the total proteins of the older leaves. Of the total N of diamino-acids fraction, they have more of arginine N and cystine N, and nearly the same rate of histidine N and lysine N. Of the total N of monoamino-acids fraction, they have less of monoamino N, and, it appears, less of non-amino N. More of tryptophane and cystine are found in the proteins of the comparatively young leaves.

(5) In accordance with the growth of the mulberry leaves, the proportion of the protein soluble in the alkaline alcohol against globulin, glutelin and albumin gets higher in the total proteins of the leaves⁽¹⁾. This fact agrees with the studies mentioned in (2), (3) and (4).

LITERATURE.

- (1) Y. Kishi: Bull. of Agricul. Chem. Soc. of Japan, Vol. IX, Nos. 1~3, 42, (1933).

Studies on the Constituents of the Mulberry Leaves, especially on the Proteins. Part XII.—A Study of the solubility of the Mulberry Leaf proteins and its Application. (pp. 363~378): By Yukitaro KISHI. (At the Katakura Research Institute of Mulberry Culture, near Hachioji City, Tokyo Prefecture Japan).

Résumé.

(1) I have studied the solubility of the proteins of the mulberry leaves, especially of the protein soluble in the alkaline alcohol and its application.

(2) The protein contained in the residue after proteins are extracted from the air-dried powders of the mulberry leaves in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide, is best resolved in the 60% boiling alcohol containing 0.3% of sodium hydroxide. And the protein in the above-mentioned residue can easily be resolved in the cold alkaline alcohol and dilute alkaline solution after it has once been extracted in the hot alkaline alcohol.

(3) The protein extracted by means of once putting in the hot alkaline alcohol the residue after protein of air-dried powders of the mulberry leaves are extracted in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide, has water (alcohol) soluble and insoluble part. The residue after the proteins in the air-dried powders of the mulberry leaves

were extracted in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide, and the residue after the water-soluble proteins were separated from the juice of the well-crushed fresh mulberry leaves, get a quantity of the water-soluble protein when each of them is artificially digested in the enzyme of the gastric juice of the silk-worms. The distribution of amino-acids and the artificial digestibility in the gastric juice of the silk-worms are the same in these water soluble and insoluble proteins. From these point, they may be judged to be the same kind of protein and quite different from the globulin, glutelin and water-soluble protein (albumin) of the mulberry seeds.

(4) In the juice of the well-crushed fresh mulberry leaves, more than half of the total proteins in the juice are the water-soluble proteins, the greater part of which may be considered the same as the alkaline-alcohol-soluble protein in the above-mentioned air-dried powders of the mulberry leaves. The distribution of amino acids in the water-soluble proteins in the juice of the well-crushed fresh leaves is different from the water-soluble protein of the mulberry seed and the dried powders of the mulberry leaves, and is much like the alkaline-alcohol-soluble protein. To be exact, the water-soluble proteins in the crushed fresh leaves must be composed of a greater part of the alkaline-alcohol-soluble protein and a part of water-soluble protein (albumin and a little globulin) mainly found in seeds.

(5) The alkaline-alcohol-soluble protein in the mulberry leaves can be determined quantitatively by means of extracting in the 60% boiling alcohol containing 0.3% of sodium hydroxide three times, each 40 minutes, the residue after the air-dried powders of the mulberry leaves were managed in water, the solution of sodium chloride, alcohol and the solution of sodium hydroxide.

In this extraction by means of the hot alkaline alcohol, we get a little of non-protein nitrogen, and, as I have mentioned in (3), we get water-soluble and water-insoluble proteins. But the water-insoluble and water-soluble proteins have the same artificial digestibility in the gastric juice of the silk-worms, and the same distribution of amino-acids. And the total proteins in the residue after the air-dried powders of the mulberry leaves were managed in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide, have the same distribution of amino-acids as the above-mentioned water-soluble and water-insoluble proteins, and differ from the proteins, such as mainly contained in the seeds. And the alkaline-alcohol-soluble protein in the air-dried powders of the mulberry leaves is insoluble in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide. Hence, it is significant to determine the alkaline-alcohol-soluble protein.

(6) The albumin and globulin in the mulberry seeds and the air-dried powders of the mulberry leaves can not only be resolved in water and 10% solution of sodium chloride, but almost also in dilute alkaline solution.

The proportion of the protein soluble in the alkaline alcohol against the proteins soluble in water, the solution of sodium chloride, alcohol, and the solution of sodium hydroxide, contained in the air-dried powders of the mulberry leaves, has much significance in sericulture⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾. From this view point, I have devised a practical method of determining the quality of the total proteins in the mulberry leaves.

In these studies I am greatly indebted to the kind advices from Professor Dr. Y. Okuda.

LITERATURE.

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| (3) | " | " | " | " | Vol. XI, Nos. 4, 77, (1935). |
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